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ARTICLE

Ring-Opening Co- and Terpolymerization of an Alicyclic Oxirane with Carboxylic Acid Anhydrides and CO_2 in the Presence of Chromium Porphyrinato and Salen Catalysts

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ABSTRACT: Copolymerization of cyclohexene oxide (CHO) with alicyclic anhydrides applying chromium tetraphenylprophyrinato (TPPCrCl, **1**) and salophen (SalophenCrCl, **2**) catalysts resulted in polyesters or poly(ester-*co*-ether)s, depending on the nature of the catalyst, presence of a cocatalyst, solvent and type of anhydride. The combination of **1** as catalyst and 4-*N*,*N*-dimethylamino-pyridine (DMAP) as cocatalyst in the copolymerization of CHO with succinic anhydride (SA), cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA) or phthalic anhydride (PA) invariably resulted in a completely alternating topology and therefore a pure polyester. Contrarily, **2** in combination with DMAP did not afford pure polyesters for the copolymerization of CHO with SA or CPrA but did render the alternating topology when CPA or PA was used as anhydride comonomer. Water proved to be an efficient bifunctional CTA affording α,ω-hydroxyl-terminated polyesters without loss of catalytic activity. When CO_2 was introduced as additional monomer to CHO and the anhydrides, both **1** and **2** in combination with DMAP as cocatalyst afforded perfect poly(ester-*co*-carbonate)s. The presence of CO_2 effectively prevents the undesirable side reaction of oxirane homopolymerization.

Introduction

Aliphatic polyesters increasingly gain attention due to their good biodegradability. Moreover, the biocompatibility of several aliphatic polyesters has augmented their use in biomedical applications such as drug delivery vesicles, bone screws and scaffolding or suture wire.[1] Generally, aliphatic polyesters are obtained by either polycondensation or ring-opening polymerization of cyclic esters. The latter route limits the polymer properties to those of the cyclic esters that are available. While the nearly endless choice of diols and diacids gives access to a much larger range of polymer properties for AABB type polyesters, their synthetic procedure of polycondensation is disadvantageous. Usually, drastic conditions are required to remove water and to drive the reaction toward high conversion and very accurate comonomer stoichiometries are necessary to obtain high molecular weight products. Ring-opening copolymerization of oxiranes and anhydrides is an alternative way to synthesize AABB type polyesters.[2−7] The catalytic coupling of oxiranes with anhydrides was first reported in the 1960s,[2] but the undesirable side-reaction of oxirane homopolymerization and the low molecular weights generally obtained impeded its popularity and its development toward a routine pathway. Until recently, the best results in terms of alternating character and molecular weight were achieved by Inoue[3] and Maeda[4] with an aluminum porphyrinato complex and magnesium diethoxide as catalysts, respectively.[5] Recently, Coates reported high molecular weight materials synthesized from several alicyclic oxiranes and anhydrides using a zinc 2-cyano-β-diketiminato complex.[6] Molecular weights up to 55 000 $g\cdot mol^{-1}$ were achieved in a perfectly alternating microstructure, which marked a breakthrough in the polyester synthesis via ring-opening copolymerization of oxiranes and anhydrides.

Carbonate segments in polyesters gained interest in the biomedical sector as these segments lower the hydrolytic degradation rate of these materials and reduce the autocatalytic degradation.[8] Besides the classical polycondensation method, poly(ester-*co*-carbonate)s can be prepared in a chain growth process by copolymerization of cyclic esters and cyclic carbonates,[8] terpolymerization of carbon dioxide, oxiranes, and lactones,[9] or terpolymerization of carbon dioxide, oxiranes, and anhydrides.[10] Whereas the copolymerization of cyclic esters and cyclic carbonates and the terpolymerization of CO_2, propylene oxide and caprolactone afford random copolymers, the terpolymerization of CO_2,[9] propylene oxide and maleic anhydride was reported to yield alternating or random poly(ester-*co*-carbonate)s.[10a,b] On the other hand, Coates and co-workers reported the formation of diblock poly(ester-*b*-carbonate)s upon terpolymerization of CO_2, cyclohexene oxide, and diglycolic anhydride using a zinc β-diketiminato catalyst.[10c] Clearly, small differences in activities of the various monomers strongly influence the polymer's topology.

Here we report on mechanistic aspects of the alternating copolymerization of the alicyclic oxirane cyclohexene oxide (CHO) with succinic anhydride (SA), cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA), and phthalic anhydride (PA) as well as the terpolymerization of carbon dioxide, CHO, and the above-mentioned anhydrides using tetraphenylporphyrinato chromium chloride (**1**) and salophen chromium chloride (**2**, where salophen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidenyl)-1,2-phenylenediamine)) as catalysts (Scheme 1) and DMAP (4-(*N*,*N*-dimethylamino) pyridine) as cocatalyst. The polymer products were subjected to an intensive MALDI−ToF−MS study to determine the polymer's

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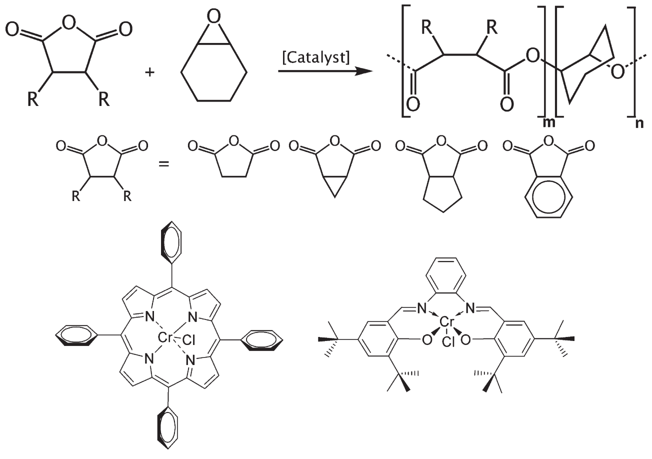
Scheme 1. Synthesis of Polyesters from Cyclohexene Oxide and Dicarboxylic Acid Anhydrides (SA, CPrA, CPA, PA) and the Catalysts 1 and 2 Used in the Copolymerization



1 **2**

topology and to derive information on chain termini to get insight in possible termination processes. The catalysts were selected based on their known ability to copolymerize cyclohexene oxide and carbon dioxide affording polycarbonates.[11,12]

Experimental Section

Reagents. SA, CPrA, PA, and CHO were purchased from Aldrich. CPA was purchased from CHESS GmbH. CHO was dried over CaH_2, distilled and stored under argon. SA was sublimed prior to use. PA, CPrA, CPA, 4-(*N*,*N*-dimethylamino)pyridine (DMAP, Aldrich), and *N*-methylimidazole (*N*-MeIm, Aldrich) were used without further purification. Complex **1** was purchased from STREM. Complex **2** was prepared according to literature procedures.[13] Toluene (Aldrich) was dried over an alumina column and stored on 4 Å molecular sieves under argon. All manipulations were performed under an inert atmosphere or in a nitrogen-filled MBraun glovebox unless stated otherwise.

Copolymerizations. Bulk: A mixture of anhydride (2.5 mmol), CHO (2.5 mmol), and catalyst (10 μmol) (+ cocatalyst (10 μmol)) was reacted in a 2 mL crimp lid vial equipped with a stirring bar placed in an aluminum heating block mounted on top of a stirrer/heating plate. The polymerization was conducted at 100 °C for 140 min. Solution: A 2 mL crimp lid vial equipped with a stirring bar was charged with a mixture of anhydride (2.5 mmol), CHO (2.5 mmol) and catalyst (10 μmol) (+ cocatalyst (10 μmol)) in toluene (0.9 mL) and was placed in an aluminum heating block mounted on top of a stirrer/heating plate. The polymerization was conducted at 100 °C for 300 min. All analyses were performed on crude samples.

Terpolymerizations. A 10 mL high-pressure reactor equipped with a stirring bar was charged with a mixture of anhydride (2.5 mmol), CHO (2.5 mmol) and catalyst (10 μmol) (+ cocatalyst (10 μmol)) in toluene (4 mL) and was put under CO_2 pressure (50 bar). Then it was placed in an aluminum heating block mounted on top of a stirrer/heating plate. The polymerization was conducted at 100 °C for 16 h. All analyses were performed on crude samples.

NMR Analysis. NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C. The solvent used was chloroform-d_1 and ^{1}H NMR spectra were referenced internally using the signal of residual solvent protons.

SEC Analysis. SEC analysis was carried out using a Waters 2695 separations module, a model 2414 refractive index detector (at 40 °C) and a model 486 UV detector (at 254 nm) in series. Injections were done by a Waters model WISP 712 autoinjector, using an injection volume of 50 μL. The columns used were a PLgel guard (5 μm particles) 50 × 7.5 mm column, followed by two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns at 40 °C in series. THF was used as eluent at a flow rate of 1.0 $mL\cdot min^{-1}$. Samples were filtered through a 0.2 μm PTFE filter (13 mm, PP housing, Alltech). For calibration polystyrene standards were used (Polymer Laboratories, M_n = 580 to 7.1 × 10^6 $g\cdot mol^{-1}$). Data acquisition and processing were performed using Waters Millennium 32 (v4.0) software.

MALDI−ToF−MS Analysis. MALDI−ToF−MS analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in THF at a concentration of 1 $mg\cdot mL^{-1}$. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 $mg\cdot mL^{-1}$. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 $mg\cdot mL^{-1}$. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode. All MALDI−ToF−MS spectra were recorded from the crude products. In-house developed software was used to characterize the polymers in detail and allowed us to elucidate the individual chain structures, the copolymer's chemical composition and topology (see Supporting Information for more details).[14]

Results and Discussion

Copolymerizations of Cyclohexene Oxide with Anhydrides. The copolymerizations were performed at 100 °C in both bulk (140 min) and in a toluene solution (300 min) with an oxirane:anhydride:catalyst(:cocatalyst) ratio of 250:250:1(:1). Selected data are given in Table 1 and Table 2. Evidently, the chromium porphyrinato or salophen complexes alone are not very active or selective catalysts. In solution hardly any activity can be observed and the copolymers obtained in bulk contain only a low percentage of ester linkages, resulting in predominantly polyether. A similar observation was made by Inoue et al., who reported mainly oligoether formation when aluminum tetraphenylporphyrinato complexes were employed without cocatalysts.[2] Conversely, with phosphonium salts as cocatalysts, the anhydride incorporation dramatically improved.[2] It has also been reported that most metal salen and porphyrinato complexes used for the oxirane−CO_2 copolymerization gave far higher activities and better selectivities in the presence of nucleophilic cocatalysts such as DMAP (4-(*N*,*N*-dimethylamino)pyridine) or *N*-MeIm (*N*-methyl imidazole).[11,12] We therefore explored the use of one of the most common cocatalyst in oxirane−CO_2 copolymerization, DMAP, as cocatalyst for **1** and **2** in the copolymerization of oxiranes and anhydrides.

The presence of DMAP as cocatalyst not only accelerated the copolymerization (especially in solution), but also strongly stimulated the formation of ester linkages. According to the ^{1}H NMR of the crude products, the copolymerization of SA and CHO with **1** and DMAP as cocatalyst afforded perfectly alternating oxirane-anhydride copolymers with high (89%) conversion. The presence of DMAP also improved the performance of **2** but with an ester content of 67% (bulk) to 73% (solution) and a moderate conversion, both selectivity and activity of **2**/DMAP were lower than for **1**/DMAP. Interestingly, the blank experiments with DMAP alone also afforded polymeric products but the conversions were significantly lower than with the catalysts **1** or **2**, especially when carried out in solution. Clearly, in combination with a nucleophilic cocatalyst the chromium complexes

Table 1. Results of Copolymerization of SA and CHO in Bulk and Solution.[a]

entry	catalyst (+ cocatalyst)	conditions	time (min)	convn CHO (%)[b]	ester bonds (%)[b]	M_n[c] (g/mol)	X_n[d]	PDI[c]
1	DMAP	bulk	140	33	53	700	7	1.2
2	DMAP	solution	300	< 5				
3	1	bulk	140	85	14	2300	23	1.9
4	1	solution	300	< 10	0			
5	1 + DMAP	bulk	140	89	100	1300	13	1.6
6	1 + DMAP	solution	300	81	100	1500	15	1.8
7	2	bulk	140	57	11	1800	18	4.2
8	2	solution	300	0				
9	2 + DMAP	bulk	140	60	67	1500	15	1.6
10	2 + DMAP	solution	300	43	73	1000	10	1.3

[a] [SA]:[CHO]:[cat]:[DMAP] = 250:250:1:1, T = 100 °C. [b] Determined by ^{1}H NMR/MALDI. [c] Determined by SEC. [d] The number-average degree of polymerization is based on the average weight of both comonomers.

Table 2. Results of Copolymerization of CHO with Different Anhydrides in Bulk and Solution[a]

entry	catalyst + cocatalyst	anhydride, condition	time (min)	convn CHO (%)[b]	ester (%)[b]	ether (%)[b]	M_n[c] (g/mol)	X_n[e]	PDI[c]
1	1 + DMAP	CPrA, bulk	140	100	100	0	5600	51	1.5
2	1 + DMAP	CPrA, solution	300	100	100	0	6600	60	1.6
3	1 + DMAP	CPA, bulk	140	100	100	0	5600	47	1.5
4	1 + DMAP	CPA, solution	300	100	100	0	4900	41	1.3
5	1 + DMAP	PA, bulk	140	61[d]	100	0	17 420	141	1.3
6	1 + DMAP	PA, solution	300	100	100	0	19 250	156	1.2
7	2 + DMAP	CPrA, bulk	140	55	70	30	4700	43	1.4
8	2 + DMAP	CPrA, solution	300	65	85	15	5700	52	1.3
9	2 + DMAP	CPA, bulk	140	72	100	0	8400	71	1.3
10	2 + DMAP	CPA, solution	300	23	100	0	3200	27	1.3
11	2 + DMAP	PA, bulk	140	66[d]	100	0	12 600	102	1.3
12	2 + DMAP	PA, solution	300	100	100	0	16 060	131	1.2

[a] [anhydride]:[CHO]:[cat]:[DMAP] = 250:250:1:1, T = 100 °C. [b] Determined by ^{1}H NMR/MALDI−ToF−MS. [c] Determined by SEC. [d] No clear solution was obtained. [e] The number-average degree of polymerization is based on the average weight of both comonomers.

1 and **2**, known to catalyze the copolymerization of carbon dioxide with oxiranes or oxetanes, are also effective catalysts for the oxirane−anhydride copolymerization affording either poly(ester-*co*-ether)s or polyesters.

Although the molecular weight shows a linear development with conversion, in all cases, the observed molecular weights are far lower than the theoretical value for a living system. This is most probably caused by intramolecular transesterification leading to the formation of cyclics or by chain transfer reactions with water (vide infra).

The polymers were analyzed by recording MALDI−ToF−MS spectra of crude products. End group determination was performed by comparing the recorded MALDI−ToF−MS spectra with simulations of the isotope patterns for given polymer structures. The MALDI−ToF−MS spectra of polymers prepared by **1** and **2** in bulk without a cocatalyst clearly show isotope patterns for chains with a significantly higher CHO than SA content. Besides the expected chloride-terminated chains, two distinct distributions, one corresponding to cyclic polymers and one consisting of linear polymer chains with α,ω-OH end groups, were observed (Figure 1a). The cyclic products are likely to be formed by intramolecular transesterification during the polymerization, whereas α,ω-hydroxy-terminated polymers most probably originate from water initiation. The MALDI−ToF−MS spectrum of the products formed by **1** in the presence of DMAP as the cocatalyst in both bulk and solution showed an m/z interval of 198 between the consecutive peaks corresponding to the addition of a [CHO + SA] repeating unit, which is in agreement with a perfectly alternating microstructure (Figure 1b). In accordance with the NMR data, for **2**/DMAP, isotope patterns for chains with a somewhat higher CHO content are present albeit that the poly(ester-*co*-ether)s contain predominantly ester linkages. End group determination for the copolymers produced by **1**/DMAP and **2**/DMAP appeared not to be straightforward. To elucidate the chain termini more information was gathered by recording MALDI−ToF−MS spectra with different cationization salts (Na^+, K^+) as well as without any cationization salt. In all cases a clear MALDI−ToF−MS spectrum was obtained with identical isotope distributions at exactly the same position in the spectrum, which implies that the chains were already ionized beforehand. Using *N*-MeIm instead of DMAP as the cocatalyst, the spectrum shifted in total −40 m/z, which is equal to the molar mass difference of DMAP and *N*-MeIm. Simulation of the isotope patterns for a chain (consisting of n SA and m CHO ($n < m$) units) end-capped at one side with the cationic cocatalyst fragment (DMAP or *N*-MeIm) and a proton as the other end group afforded a perfect fit of the isotope distributions. This observation strongly suggests the presence of zwitterionic chain structures and also explains the formation of cyclic structures.[15,16] Similar zwitterionic chain structures have also been proposed for the copolymerization of CHO and CO_2 with metal salen catalysts in combination with nucleophilic cocatalysts[11,12] and for the ring-opening polymerization of lactones by organic catalysts.[16] The polymer prepared with **1**/DMAP showed a structure with exactly n SA and n+1 CHO units (Figure 1b), indicating that the oxirane is the preferred monomer to react with the DMAP (or *N*-MeIm).

Although the MALDI−ToF−MS spectra exclusively show DMAP (or *N*-MeIm) end-capped chains, it does not at all mean that these are the only end groups present. It should be noted that only a fraction of uncharged chains are cationized by the added cationization salt and will be visible in the MALDI−ToF−MS, while *all* DMAP end-capped polymers are charged. Hence, the latter will completely suppress the originally uncharged chains in the MALDI−ToF−MS spectra.

The conversions of SA and CHO with **1**/DMAP and **2**/DMAP were rather low, especially in solution. It was argued that in case ring-opening of the anhydride is the rate-determining step, increasing the ring strain in the anhydride

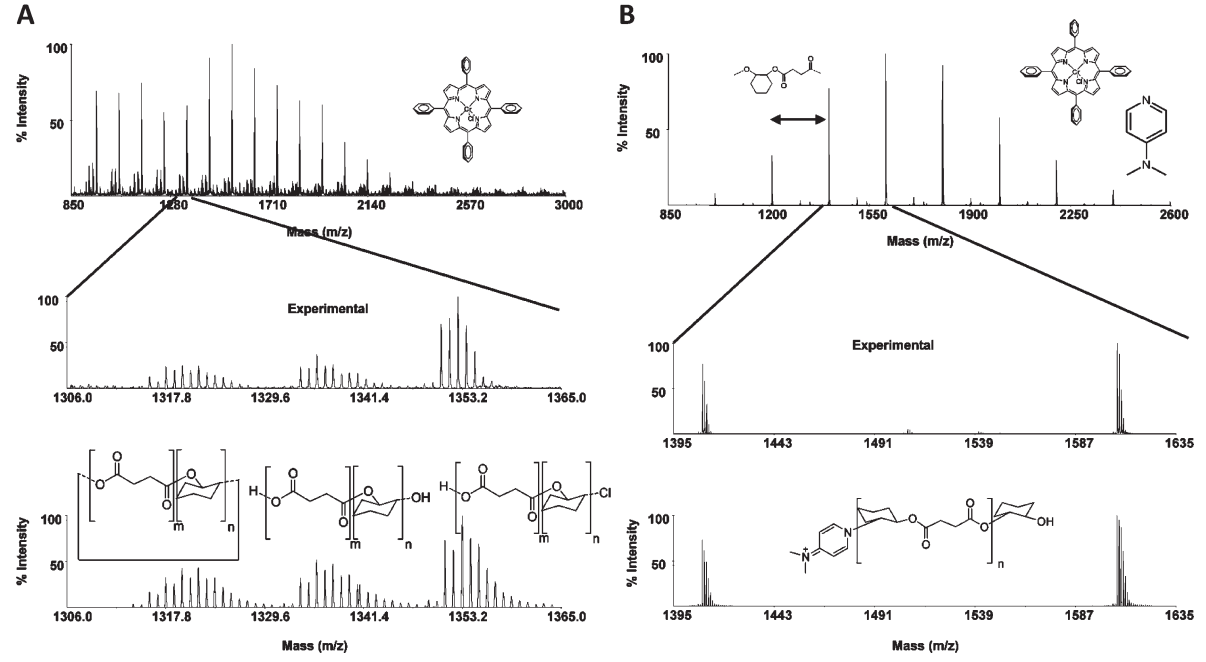


Figure 1. MALDI−ToF−MS spectrum of SA−CHO copolymer synthesized in bulk using (a) **1** and (b) **1**/DMAP.

might increase its reactivity, which might lead to more alternating copolymers with higher molecular weights. The influence of increasing the reactivity of the anhydride monomer was therefore studied for both catalysts by replacing the aliphatic succinic anhydride by the alicyclic anhydrides cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA) and phthalic anhydride (PA). Selected data are given in Table 2.

Except for the bulk polymerization of PA, which did not give a clear solution at 100 °C as a result of the poor solubility and high melting point of PA, all polymerizations catalyzed by **1**/DMAP gave 100% conversion. Interestingly, the increased ring strain also results in an increase in the number-average degree of polymerization (X_n) compared to the CHO + SA copolymerization at similar conversion. The catalytic system **1**/DMAP gives perfectly alternating copolymers with all three anhydrides both in bulk and solution. Similar to what was found for the copolymerization of CHO and SA, **2**/DMAP shows a somewhat lower selectivity and activity for these anhydrides compared to **1**/DMAP. For example, for the copolymerization of CPrA and CHO in both bulk and solution still some ether bonds could be found. On the other hand, the copolymerization of CHO and CPA or PA using **2**/DMAP afforded perfectly alternating polymer chains with a significantly higher degree of polymerization than with SA (Table 2). This can clearly be seen when comparing the contour plots (Figure 2) constructed from the recorded MALDI−ToF−MS spectra of copolymers obtained from CHO and SA or CPrA, catalyzed by **1**/DMAP and **2**/DMAP, respectively. These plots reveal the perfectly alternating character of the copolymers when prepared with **1**/DMAP, while the polymers obtained from **2**/DMAP clearly show a somewhat higher CHO content for all polymer chains indicating that **2**/DMAP catalyzed polymerization affords random poly(ester-*co*-ether)s rather than poly(ester-*b*-ether) block copolymers.

Although the number-average degree of polymerization (X_n) is significantly higher than for CHO + SA, the molecular weights of the CHO copolymers with CPrA, CPA, and PA are still substantially lower than the theoretical values expected from the monomer to initiator ratio for the observed conversion. We exclude the possibility of transesterification as the main cause of this discrepancy since the molar mass distributions of the synthesized polymers are relatively narrow (≤ 1.6). Alternatively, the formation of ring structures too small to be detected by MALDI as a result of a back-biting process was also excluded since first $^1H/^{13}C$ NMR and ESI-MS did not reveal the presence of such species and second the polymer yield was in good agreement with the conversion. Supported by the presence of α,ω-hydroxyl terminated polymer chains in the MALDI−ToF−MS, we therefore assume that water present in small amounts in the system, or the diacid formed upon reaction of the anhydride with water, acts as a very effective chain transfer agent for the chromium catalyst system (vide infra).

MALDI−ToF−MS spectra of the copolymers derived from CHO plus CPrA or CPA obtained by **2**/DMAP revealed the presence of DMAP end-capped chains. The products prepared with **1**/DMAP show different end groups in the MALDI−ToF−MS. Apart from hydroxyl-terminated chains which were dominating the spectrum, a low molecular weight, low intensity distribution could be attributed to chloride-terminated chains. The α,ω-hydroxyl-terminated species were attributed to the presence of water in the system. Why the end groups observed by MALDI−ToF−MS of the copolymers derived from CHO plus CPrA and CPA are different for the seemingly similar systems **1**/DMAP and **2**/DMAP is not clear, but it is likely that even small deviations in the relative concentration of the different end groups are magnified by MALDI−ToF−MS.

It is interesting to note that the α,ω-hydroxyl end-capped polymer chains display a bimodal distribution, in which two distributions differ by approximately a factor of 2 in molecular weight. This is clearly visible in for example the MALDI−ToF−MS spectrum of the copolymer of CPA and CHO. Size exclusion chromatograms reveal the same bimodal distribution (Figure 3). The observation of a similar sharp bimodal behavior has been reported for ethylene oxide−phthalic anhydride copolymerization and for oxirane − CO_2 copolymerizations.[3b,11,17,18] Initially, the possibility was raised that the bimodal behavior can derive from the simultaneous growth of two polymer chains on each side of

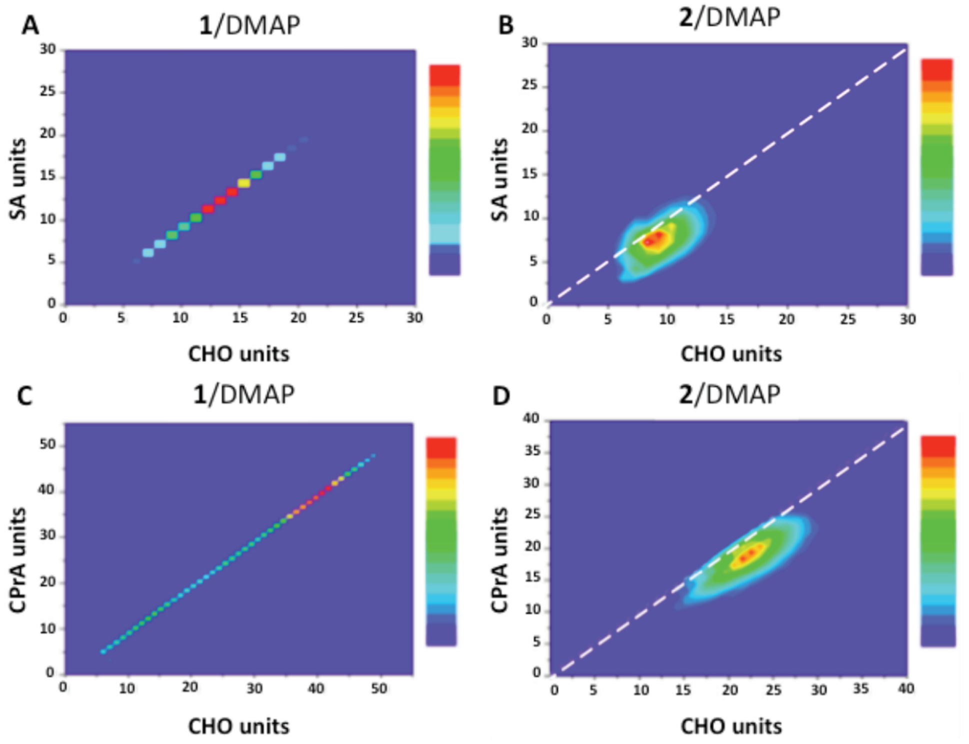


Figure 2. Contour plots of MALDI−ToF−MS spectra of polyesters synthesized from (a) SA + CHO by **1**/DMAP, (b) SA + CHO by **2**/DMAP, (c) CPrA + CHO by **1**/DMAP, and (d) CPrA + CHO by **2**/DMAP.

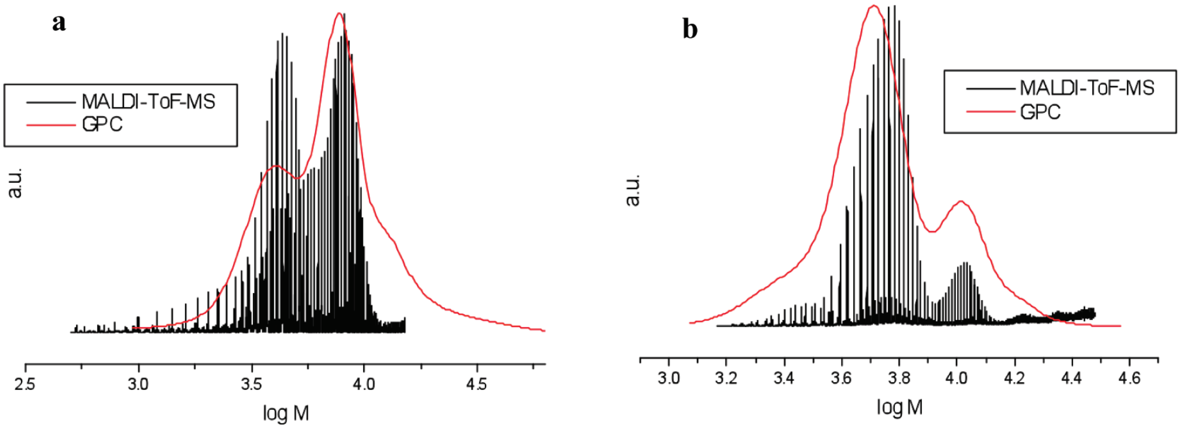


Figure 3. Overlay of SEC and MALDI−ToF−MS spectra for (a) CPrA + CHO by **1**/DMAP (Table 2, entry 3) and (b) CPA + CHO by **1**/DMAP (Table 2, entry 6).

respectively a metalloporphyrin and metallosalen plane.[3b,11] However, a recent study by Darensbourg excluded this possibility.[19] Recently, a similar bimodality has been reported and studied by Sugimoto and Kuroda in the alternating copolymerization of cyclohexene oxide with CO_2 using DMAP/TPPCoCl.[17] They attributed this behavior to water initiation occurring even after intensive drying. In addition, the bimodality in molecular weight distributions is not limited to metal porphyrin and salen complexes, but is also observed for zinc β-diketiminato complexes. Eberhardt et al. reported a narrow yet bimodal molecular weight distribution for the polymerization of cyclohexene oxide with CO_2 employing a β-diketiminato zinc sulfinate complex.[18]

Keeping in mind that alcohols including hydroxyl-terminated polymers can behave as effective CTAs[20] producing immortal catalyst systems,[21] it is most likely that water in the system or the diacid formed by reaction of water and the anhydride acts as a bifunctional chain transfer agent responsible for the overall lower molecular weight and the bimodal distribution of α,ω-dihydroxyl functionalized polymer chains. This also explains the fact that the two distributions differ by approximately a factor of 2 in molecular weight assuming that low and high molecular weight chains are the result of mono- and bimetallic systems, respectively. The positive side of this result is that water might provide a simple tool to produce low molecular weight α,ω-difunctional polyester resins suitable for e.g. coating applications. To confirm this hypothesis, the copolymerizations of CHO + SA and CHO + PA catalyzed by **2** were carried out in the presence of 10 equiv of water. Although no visible effect on the already low molecular weight of the CHO + SA copolymers could be observed, for the CHO + PA copolymerization a significant reduction of molecular weight as the result of the additional water is indeed observed. Worth mentioning is the fact that the catalytic activity is not at all affected by the presence of additional water. Whereas zinc-based catalysts such as

Scheme 2. Synthesis of Poly(ester-*co*-carbonate) from Cyclohexene Oxide, Carbon Dioxide, and Alicyclic Anhydrides

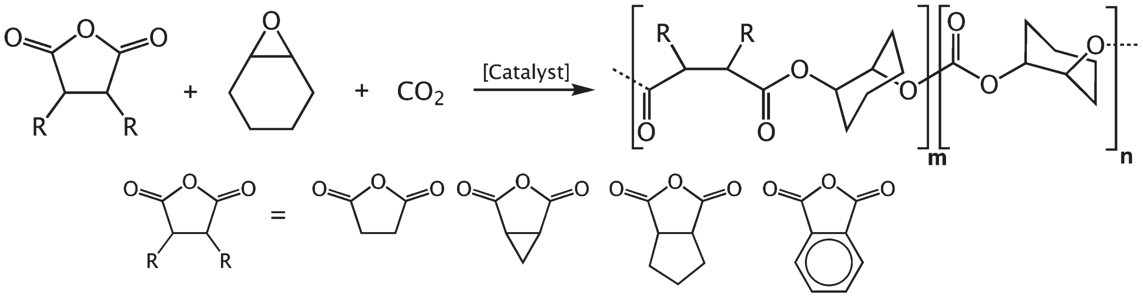


Table 3. Results of Terpolymerizations of CHO, CO_2 and the Anhydrides SA CPrA, CPA, and PA.[a]

entry	catalyst	anhydride	ratio CHO:Anh	convn[b](CHO %)	M_n (g/mol)	PDI[c]	ester (%)[d]	carbonate (%)[d]	ether (%)[d]
1	**1**	SA	1:1	95	1960	1.5	95	0	5
2	**1**	SA	2:1	88	1616	1.5	70	14	16
3	**1**	CPrA	2:1	100	3200	1.1	65	35	0
4	**1**	CPA	2:1	100	10 260	1.2	65	35	0
5	**1**	PA	1:1	99	16 075	1.6	71	29	0
6	**1**	PA	2:1	100	13 220	1.4	51	49	0
7	**2**	SA	1:1	93	1890	1.4	96	0	4
8	**2**	SA	2:1	69	2100	1.5	82	8	10
9	**2**	SA	4:1	62	2700	1.5	75	12	13
10	**2**	SA	8:1	47	2320	1.7	54	27	19
11	**2**	CPrA	1:1	90	1100	1.1	100	0	0
12	**2**	CPrA	2:1	96	2600	1.1	65	35	0
13	**2**	CPrA	4:1	97	3800	1.1	60	40	0
14	**2**	CPrA	8:1	93	5800	1.1	40	60	0
15	**2**	CPA	1:1	100	7000	1.2	100	0	0
16	**2**	CPA	2:1	87	6600	1.3	61	39	0
17	**2**	CPA	4:1	87	7500	1.3	50	50	0
18	**2**	CPA	8:1	95	7700	1.4	19	81	0
19	**2**	PA	1:1	96	14 600	1.3	100	0	0
20	**2**	PA	2:1	95	15 570	1.3	58	42	0
21	**2**	PA	4:1	93	11 800	1.6	35	65	0
22	**2**	PA	8:1	93	10 880	1.6	16	84	0

[a] Conditions: 50 bar CO_2, [anhydride]:[CHO]:[cat]:[DMAP] = 250:250:1:1, T = 80 °C, toluene, 18 h. [b] Determined by ^1H NMR. [c] Determined by SEC. [d] Ratio of ester:carbonate:ether in the copolymer determined by MALDI−ToF−MS. Reaction time = 16 h.

β-ketiminato zinc system tend to form inactive hydroxides with water,[22] the chromium catalysts **1** and **2** are presumed to form hydroxyl or μ-oxo species which remain active. This opens the opportunity to produce well-defined α,ω-dihydroxyl polyesters with a narrow PDI in a very convenient way.

Terpolymerization of oxiranes, anhydrides and CO_2. Since **1**/DMAP and **2**/DMAP provide active catalyst systems for the copolymerization of CHO and anhydrides and are known to be effective catalysts for the copolymerization of CHO and carbon dioxide, we attempted the terpolymerization of carbon dioxide, CHO and anhydrides (Scheme 2). Terpolymerizations were performed overnight at 80 °C in toluene using 50 bar of CO_2 pressure (Table 3).

The polymeric products were characterized by ^1H NMR, SEC, and MALDI−ToF−MS. The reactions were considerably slower than the corresponding copolymerizations in the absence of CO_2 and overnight runs were required to reach high conversion. As for the copolymerization of CHO and anhydrides, **1**/DMAP shows a somewhat higher activity than **2**/DMAP. To get insight in the relative reactivity of the anhydride and carbon dioxide, reactions with equimolar amounts of CHO and anhydride were carried out in the presence of CO_2. Whereas **2**/DMAP gives close to 100% polyester, **1**/DMAP produces significant amounts of carbonate functionalities with equimolar amounts of oxirane and anhydride. Clearly, not only the reactivity ratio of the monomers but also the affinity of the catalyst plays a role in the ester versus carbonate formation. Nevertheless, the ester formation is for both catalysts clearly favored. At higher CHO:anhydride ratios both catalysts produce poly(ester-carbonate)s. On the basis of the observed difference in reactivity, block copolymers are expected to be formed similar as Coates found for the zinc-catalyzed terpolymerization of CHO plus CO_2 and anhydrides.[10c]

Generally, DSC can provide valuable information about the topology (block versus random) of a copolymer. A blocky structure should give two T_g's and a random copolymer just one T_g. This is true when the two phases are not miscible. DSC data have been collected of both the terpolymers (CO_2 + CHO + SA; CO_2 + CHO + PA) and the blends of the corresponding copolymers (CO_2 + CHO; SA + CHO; PA + CHO) and it appears that the copolymers are perfectly miscible as they show only a single T_g. Therefore, DSC does not give us a conclusive answer about the topology of the polymers (see Supporting Information). However, Figure 4 clearly supports the presence of a blocky topology. In Figure 4a, the relative content of ester and carbonate functionalities versus CHO conversion is plotted. It can clearly be seen that carbonate functionalities are hardly being built in until 45% of CHO conversion has been reached, which corresponds to 90% conversion of the anhydride. This means that approximately 90% of the anhydride is built-in into the polymer as part of a pure polyester block. Although the number of data points at low conversion is limited, Figure 4b supports this assumption. After approximately 40−50% CHO conversion, the slope of the curve lowers in reasonably good agreement with the difference in mass of the repeating units (phthalic anhydride + CHO versus CO_2 + CHO).

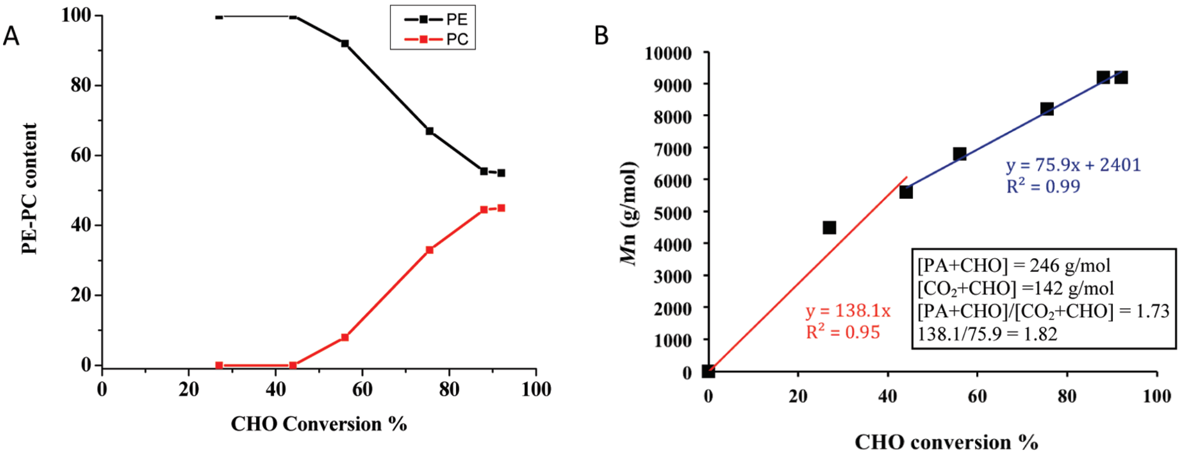


Figure 4. (a) Development of the ester and carbonate content versus conversion of CHO for the terpolymerization of phthalic anhydride, cyclohexene oxide (2:1) and CO_2 with salophenCrCl/DMAP. (b) Plot of M_n versus conversion of the terpolymerization of phthalic anhydride, cyclohexene oxide (2:1 ratio) and CO_2 with salophen−CrCl/DMAP.

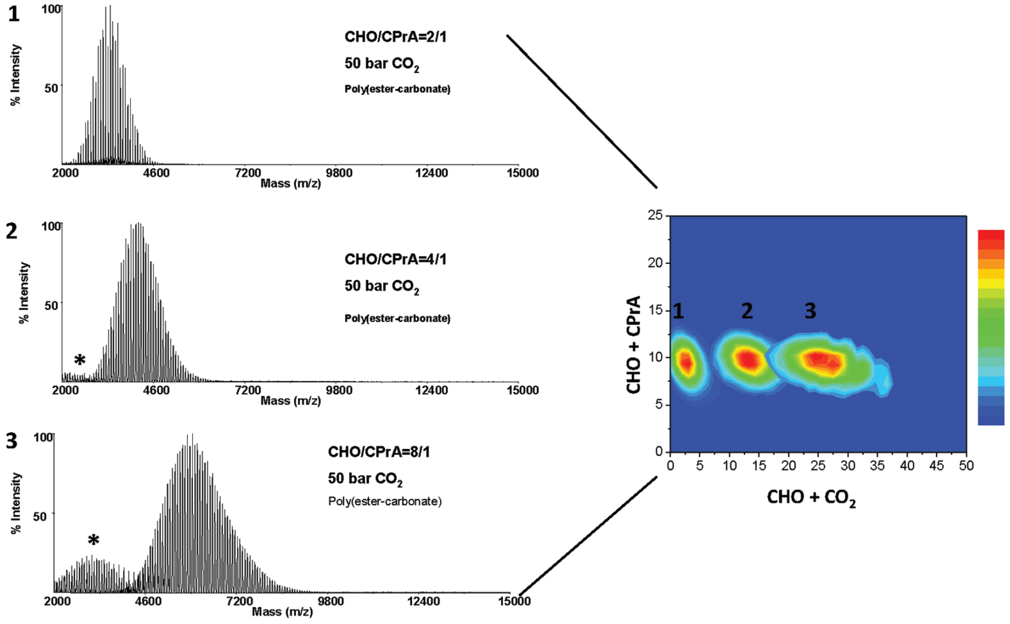


Figure 5. MALDI−ToF−MS spectra of poly(ester-*co*-carbonate) synthesized by CHO, CO_2, and CPrA catalyzed by **2**/DMAP. * = poly(cyclohexene carbonate).

The polyesterblock is expected to precede a tapered structure that gradually transfers into a polycarbonate block.

Interestingly, the **2**/DMAP-catalyzed copolymerization of equal amounts of CHO and CPrA in the presence of CO_2 afforded pure polyester, while the same reaction *in the absence* of CO_2 gave between 15 and 30% of ether linkages. This clearly demonstrates the ability of CO_2 to effectively suppress the formation of ether functionalities. It was found that even 1 bar of CO_2 is enough to completely suppress the formation of ether linkages. Probably, coordination of CO_2 lowers the metal's Lewis acidity enough to prevent subsequent ring-opening of oxiranes. Furthermore, the fact that an equimolar ratio of oxirane and anhydride affords polyester without any carbonate functionalities also demonstrates the higher reactivity of the anhydrides compared to CO_2, although competitive coordination of CO_2 is likely to be responsible for the lower polymerization rate. To obtain polymers with a significant number of carbonate functionalities a rather high oxirane:anhydride ratio or long reaction times and a high carbon dioxide pressure are required. For example, reducing the pressure to 10 bar already afforded pure polyester as the sole polymer product plus unreacted CHO.

The contour plots of catalytic runs with decreasing anhydride to oxirane ratio, by increasing the CHO concentration, show the changing ratio of ester to carbonate bonds in the terpolymer while the absolute amount of ester functionalities remains unchanged (Figure 5). A closer look at Table 3 and Figure 5 displays a discrepancy between the CHO conversion and the ratio of carbonate to ester bonds. Despite the fact that high CHO conversions are reached, the ester:carbonate ratio is invariably higher than expected based on the initial ratio of anhydride and oxirane. This inconsistency is caused by the formation of cyclohexene carbonate (formed by back biting) and the presence of some free polycarbonate (detected by MALDI−ToF−MS, see Figure 5). Simulation of the MALDI−ToF−MS spectra revealed the presence of beforehand-ionized DMAP-terminated chains as well as water or chloride initiated chains. As for the polyesters (Figure 2) the DMAP-end-capped polymers contain one additional cyclohexene oxide unit, indicative for the preference of DMAP to react with CHO rather than the anhydride or carbon dioxide (vide supra).

Conclusions

While **1**, **2**, and DMAP alone are poor catalysts for the CHO−anhydride copolymerization mainly giving low molecular weight ester-enriched polyethers, the combination of **1** and **2** with DMAP gives potent catalysts for the alternating CHO−anhydride copolymerization to the corresponding polyesters. Catalyst **1**/DMAP is more active and in most cases more selective than **2**/DMAP, whereas the opposite was observed for cyclohexene oxide−CO_2 copolymerization.[11] Using bicyclic anhydrides with an increased ring strain compared to SA leads to an increase in the reaction rate, degree of polymerization and selectivity for perfectly alternating copolymers. While the copolymerization of CHO with bicyclic anhydrides catalyzed by **1**/DMAP afforded perfectly alternating structures, the copolymerization of CHO and CPrA catalyzed by **2**/DMAP still gave some ether functionalities in the predominantly polyester. Introduction of a third monomer, CO_2, resulted in poly(ester-*co*-carbonate)s. The anhydride is clearly more reactive than CO_2 as can be concluded from the fact that no or minor amounts (in the case of **1**/DMAP) of carbon dioxide is built in when the anhydride:oxirane ratio equals 1:1. Interestingly, CO_2 effectively prevents the formation of ether functionalities, as was in some cases observed in the absence of CO_2.

For all co- and terpolymerizations, the molecular weight shows a linear correlation with conversion and the PDI is ≤ 1.6 indicating a controlled behavior. However, the observed molecular weights are significantly lower than the theoretically expected values. It was proven that water in the system, often thought of as a catalyst poison, is actually a very efficient bifunctional chain transfer agent, which does not affect the catalytic activity and results in a bimodal distribution of α,ω-hydroxyl-functionalized polymers differing by a factor of 2 in molecular weight.

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Supporting Information Available: Figures showing MALDI−ToF−MS spectra and M_n, conversion, and time plots of polymerizations and tables of T_g values and copolymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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